

Rate Law Worksheet Side 1

1. For the reaction, $2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$, the rate of formation of $\text{NO}_2(\text{g})$ is $4.0 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$.

- Calculate the rate of disappearance of $\text{N}_2\text{O}_5(\text{g})$
- Calculate the rate of appearance of $\text{O}_2(\text{g})$.

$$a \quad 4.0 \times 10^{-3} \frac{\text{M NO}_2}{\text{s}} \times \frac{1 \text{ mol N}_2\text{O}_5}{2 \text{ mol NO}_2} = -2.0 \times 10^{-3} \frac{\text{M N}_2\text{O}_5}{\text{s}}$$

$$b \quad 4.0 \times 10^{-3} \frac{\text{M NO}_2}{\text{s}} \times \frac{1 \text{ mol O}_2}{4 \text{ mol NO}_2} = 1.0 \times 10^{-3} \frac{\text{mol O}_2}{\text{L s}}$$

2. The reaction $2 \text{NO}(\text{g}) + 2 \text{H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$ is found experimentally to be second order in $\text{NO}(\text{g})$ and first-order in $\text{H}_2(\text{g})$.

- Write the *rate law* for the reaction.
- What is the overall order of the reaction?
- What are the units for the rate constant k ?
- If $[\text{NO}]$ is doubled (while keeping $[\text{H}_2]$ constant), by what factor will the reaction rate increase?
- If $[\text{H}_2]$ is doubled (while keeping $[\text{NO}]$ constant), by what factor will the reaction rate increase?

$$a \quad \text{Rate} = k [\text{NO}]^2 [\text{H}_2]$$

b 3

$$c \quad \frac{1}{\text{M}^2 \text{ s}} \text{ or } \text{M}^{-2} \text{ s}^{-1} \text{ or } \text{mol}^{-2} \text{ L}^2 \text{ s}^{-2}$$

$$d \quad \text{go up by factor of 4} \quad (2)^2 = 4$$

$$e \quad \text{go up by factor of 2} \quad (2)^1 = 2$$

RATE LAWS WORKSHEET (con't)

1. Consider the reaction: $2 \text{NO(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{NO}_2\text{(g)}$

The following data were obtained from three experiments using the method of initial rates:

	Initial [NO] mol L ⁻¹	Initial [O ₂] mol L ⁻¹	Initial rate NO mol L ⁻¹ s ⁻¹
Experiment 1	0.010	0.010	2.5×10^{-5}
Experiment 2	0.020	0.010	1.0×10^{-4}
Experiment 3	0.010	0.020	5.0×10^{-5}

- Determine the order of the reaction for each reactant.
- Write the rate equation for the reaction.
- Calculate the rate constant.
- Calculate the rate (in mol L⁻¹s⁻¹) at the instant when [NO] = 0.015 mol L⁻¹ and [O₂] = 0.0050 mol L⁻¹.
- At the instant when NO is reacting at the rate of 1.0×10^{-4} mol L⁻¹s⁻¹, what is the rate at which O₂ is reacting and NO₂ is forming?

a. $\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k [\text{NO}]_2^m [\text{O}_2]_2^n}{k [\text{NO}]_1^m [\text{O}_2]_1^n}$ For NO $\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[\text{NO}]_2^m}{[\text{NO}]_1^m} = \frac{1.0 \times 10^{-4} \text{ M}}{2.5 \times 10^{-5} \text{ M}} = \frac{(0.020 \text{ M})^m}{(0.010 \text{ M})^m} = 4 = (2)^m \Rightarrow m = 2$

For O₂ $\frac{\text{Rate}_3}{\text{Rate}_1} = \frac{[\text{O}_2]_3^n}{[\text{O}_2]_1^n} = \frac{5.0 \times 10^{-5} \text{ M}}{2.5 \times 10^{-5} \text{ M}} = \frac{(0.020 \text{ M})^n}{(0.010 \text{ M})^n} = 2 = (2)^n \Rightarrow n = 1$

b. $\text{Rate} = k [\text{NO}]^2 [\text{O}_2]$

c. $k = \frac{\text{Rate}}{[\text{NO}]^2 [\text{O}_2]} = \frac{2.5 \times 10^{-5} \text{ s}^{-1}}{(0.01 \text{ M})^3} = 25 \text{ M}^{-2} \text{ s}^{-1}$

d. $\text{Rate} = (25 \text{ M}^{-2} \text{ s}^{-1}) (0.015 \text{ M})^2 (0.0050 \text{ M}) = 2.81 \times 10^{-5} \text{ M}$

e. $\text{O}_2 = 1.0 \times 10^{-4} \text{ M} \times \frac{1 \text{ mol O}_2}{2 \text{ mol NO}} = 5.0 \times 10^{-5} \text{ M}$
 $\text{NO}_2 = 1.0 \times 10^{-4} \text{ M} \times \frac{2 \text{ mol NO}_2}{1 \text{ mol NO}} = 1.0 \times 10^{-4} \text{ M}$

2. The reaction $2 \text{NO(g)} + 2 \text{H}_2\text{(g)} \rightarrow \text{N}_2\text{(g)} + 2 \text{H}_2\text{O(g)}$ was studied at 904 °C, and the data in the table were collected.

	Initial [NO] mol L ⁻¹	Initial [H ₂] mol L ⁻¹	Initial rate N ₂ mol L ⁻¹ s ⁻¹
Experiment 1	0.420	0.122	0.136
Experiment 2	0.210	0.122	0.0339
Experiment 3	0.210	0.244	0.0678
Experiment 4	0.105	0.488	0.0339

- Determine the order of the reaction for each reactant.
- Write the rate equation for the reaction.
- Calculate the rate constant at 904 °C.
- Find the rate of appearance of N₂ at the instant when [NO] = 0.350 M and [H₂] = 0.205 M.

a. $\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{[\text{NO}]_1^m}{[\text{NO}]_2^m} = \frac{0.136 \text{ M}}{0.0339 \text{ M}} = \frac{(0.420 \text{ M})^m}{(0.210 \text{ M})^m} = 4 = (2)^m \Rightarrow m = 2$ $\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{0.0678 \text{ M}}{0.0339 \text{ M}} = \frac{(0.244 \text{ M})^n}{(0.122 \text{ M})^n} = 2 = (2)^n \Rightarrow n = 1$

b. $\text{Rate} = k [\text{NO}]^2 [\text{H}_2]$

c. $k = \frac{\text{Rate}}{[\text{NO}]^2 [\text{H}_2]} = \frac{0.136}{(0.420)^2 (0.122)} = 6.3 \text{ M}^{-2} \text{ s}^{-1}$ $\text{Rate} = (6.3) (0.350 \text{ M})^2 (0.205 \text{ M}) = 0.158 \text{ M s}^{-1}$

Integrated Rate Law (Note: You will need to use Excel for this homework assignment)

1. The following data were obtained for the gas-phase decomposition of nitrogen dioxide at 300°C,



Time (s)	[NO ₂](M)
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

Is the reaction zero, first, or second order?

2nd Order $k = 0.5431 \text{ M}^{-1}\text{s}^{-1}$

Considering the same reaction above, but with a starting concentration of nitrogen dioxide of 0.500M. What would be the remaining concentration of NO₂ after 0.500 hr?

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

$$0.500 \text{ hr} \times \frac{60 \text{ min}}{1 \text{ hr}} \times \frac{60 \text{ s}}{1 \text{ min}} = 1800 \text{ s}$$

$$\frac{1}{[A]} = (0.5431)(1800 \text{ s}) + \frac{1}{0.5 \text{ M}}$$

$$\frac{1}{[A]} = 980 \quad [A] = 0.00102 \text{ M}$$

2. The first-order rate constant for the decomposition of N₂O₅, $\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$, at 70°C is $6.82 \times 10^{-3} \text{ s}^{-1}$.

Suppose we start with 0.00250 moles of N₂O₅ in a constant volume of 2.0L.

a) How many moles of N₂O₅ will remain after 2.5 min?

b) How many minutes will it take for the quantity of N₂O₅ to drop to 0.010 mol?

c) What is the half-life of N₂O₅ at 70°C?

a) $2.5 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} = 150 \text{ s}$

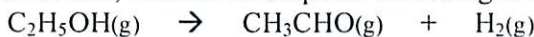
b) $\ln\left(\frac{0.010 \text{ mol}}{2.0 \text{ L}}\right) = -(6.82 \times 10^{-3} \text{ s}^{-1})t + \ln\left(\frac{0.00250 \text{ mol}}{2.0 \text{ L}}\right)$

$$\ln[A] = (-6.82 \times 10^{-3} \text{ s}^{-1})(150 \text{ s}) + \ln\left(\frac{0.00250 \text{ mol}}{2.0 \text{ L}}\right)$$

c) $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.82 \times 10^{-3} \text{ s}^{-1}} = 102 \text{ s}$

$$\ln[A] = -7.71 \quad [A] = 0.000449 \text{ M} \times 2.0 \text{ L} = 0.000898 \text{ mol N}_2\text{O}_5$$

3. At 500K in the presence of a copper surface, ethanol decomposes according to the equation:



The pressure of the ethanol was measured as a function of time and the following data were obtained:

Time (s)	[C ₂ H ₅ OH](torr)
0.0	250.
100.0	237
200.0	224
300.0	211
400.0	198
500.0	185

$$[A] = -kt + [A]_0$$

$$= -(1.71 \times 10^{-4} \text{ atm/s})(900 \text{ s}) + [0.3289 \text{ atm}]$$

$$= 0.1751 \text{ atm} \times \frac{760 \text{ torr}}{1 \text{ atm}} = 133 \text{ torr}$$

See graph Order
or decrease 13 torr every 100s

Since the pressure of a gas is directly proportional to the concentration of a gas, we can express the rate law for a gaseous reaction in terms of partial pressures. Using the data above, deduce the rate law, the integrated rate law, and the value of the rate constant, all in terms of pressure units in atm and time in seconds. Predict the pressure of C₂H₅OH after 900. s from the start of the reaction.

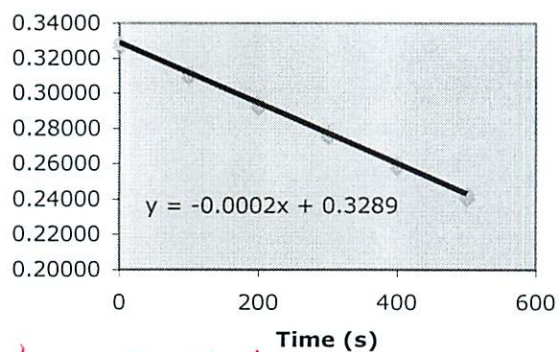
Rate = k , $[A] = -kt + [A]_0$ $k = -\text{slope} = 2 \times 10^{-4} \text{ atm/s}$

$$\text{or } k = \left(\frac{[A] - [A]_0}{t} \right) = \frac{0.31184 \text{ atm} - 0.3289 \text{ atm}}{100 \text{ s}} = 1.71 \times 10^{-4} \text{ atm/s}$$

Question 3

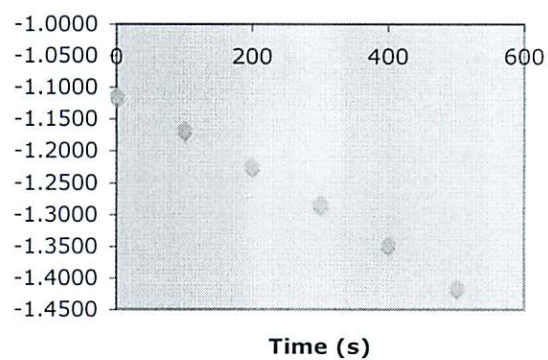
Time (s)	P C ₂ H ₅ OH(torr)	P C ₂ H ₅ OH(atm)	lnC ₂ H ₅ OH	1/C ₂ H ₅ OH
0	250	0.32895	-1.1119	3.040
100	237	0.31184	-1.1653	3.207
200	224	0.29474	-1.2217	3.393
300	211	0.27763	-1.2815	3.602
400	198	0.26053	-1.3451	3.838
500	185	0.24342	-1.4130	4.108

Pressure vs. Time

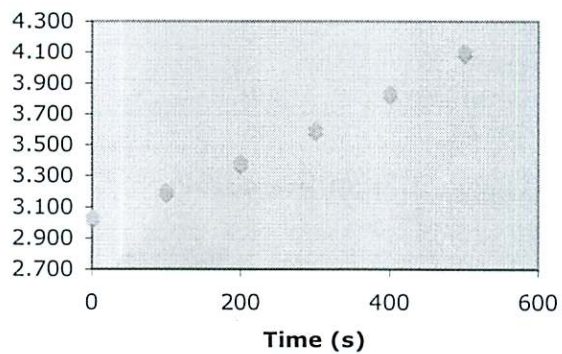


linear so order

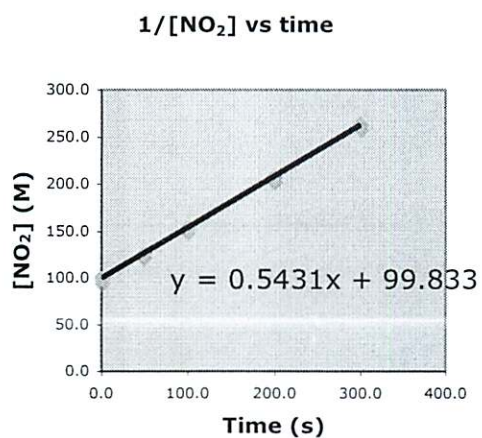
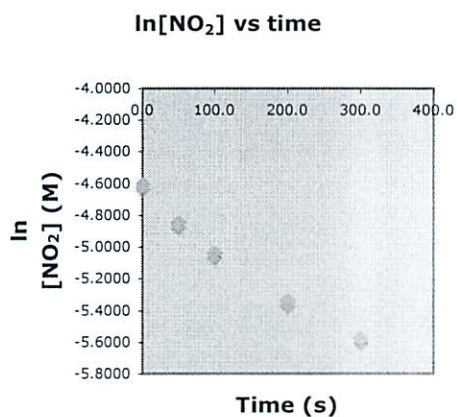
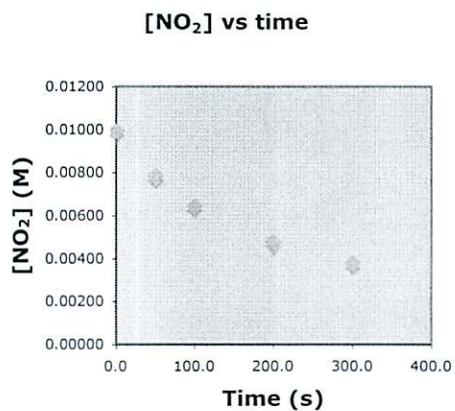
ln Pressure vs. Time



Pressure vs. Time



Question 1			
Time (s)	[NO ₂] (M)	ln[NO ₂]	1/[NO ₂]
0.0	0.01000	-4.6052	100.0
50.0	0.00787	-4.8447	127.1
100.0	0.00649	-5.0375	154.1
200.0	0.00481	-5.3371	207.9
300.0	0.00380	-5.5728	263.2



← linear so 2nd order

Integrated Rate Law Review and Half Life

1. Match the correct equation with the reaction order by writing zero, first, or second in each blank.

$$\begin{array}{ll} \frac{1}{[A]_t} - \frac{1}{[A]_0} = kt & \text{2nd} \quad t_{1/2} = \frac{[A]_0}{2k} \quad 0 \\ [A]_t - [A]_0 = -kt & 0 \quad t_{1/2} = \frac{1}{k[A]_0} \quad \text{2nd} \\ \ln[A]_t - \ln[A]_0 = -kt & \text{1st} \quad t_{1/2} = \frac{0.693}{k} \quad \text{1st} \end{array}$$

2. Write the first order integrated rate law in its "division" form.

$$\frac{\ln[A]_t}{[A]_0} = -kt$$

3. Rearrange the integrated rate laws into equations for a line: $y = mx + b$. For each reaction order, identify what type of plot (y vs x) will give a straight line, and identify what the slope of the resulting line corresponds to.

	y	vs	x	slope
zero	$[A]$		t	$-k$
first	$\ln[A]$		t	$-k$
second	$1/[A]$		t	k

4. Identify whether each of the following statements about half-lives refers to zero, first, and/or second order reactions.

1st $t_{1/2}$ is constant during a rxn.

2nd $t_{1/2}$ varies during a rxn, getting longer as the rxn proceeds.

0 $t_{1/2}$ varies during a rxn, getting shorter as the rxn proceeds.

1st 2nd 0 For a given rxn, two scientists will get different $t_{1/2}$ values experimentally if they use different initial concentrations.

1st For a given rxn, two scientists will get the same $t_{1/2}$ value experimentally, regardless of initial concentration.

5. Which of the following data sets corresponds to a second order reaction?

<u>A</u>		<u>B</u>		<u>C</u>	
$[A](M)$	$t(s)$	$[A](M)$	$t(s)$	$[A](M)$	$t(s)$
100	0	100	0	100	0
50	10	50	10	50	10
25	20	25	30	25	15

See graph

6. It takes 30.0 min for the concentration of a reactant in a second order reaction to drop from 0.40 M to 0.30 M.

- a) What is the value of the rate constant for this reaction and its units?
b) How long will it take for the concentration to drop from 0.40 M to 0.20 M?

$$a \quad 30.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} = 1800 \text{ s}$$

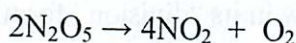
$$\frac{1}{[0.30 \text{ M}]} = k(1800 \text{ s}) + \frac{1}{[0.40 \text{ M}]}$$

$$k = 4.63 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$$

$$b \quad \frac{1}{[0.20 \text{ M}]} = (4.63 \times 10^{-4})t + \frac{1}{[0.40 \text{ M}]}$$

$$t = 5400 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = 90 \text{ min}$$

7. For the first order reaction:



$$\ln[A] = -kt + \ln[A]_0$$

- a) If 20.0% of the initial N_2O_5 decomposes in 2.10 hr, what is the rate constant?
b) What is the half-life of the reaction?
c) If the initial concentration of N_2O_5 was 0.222 M, what concentration remains after 24 hr?

$$(a) \quad 2.10 \text{ hr} \times \frac{3600 \text{ s}}{1 \text{ hr}} = 7.56 \times 10^3 \text{ s}$$

$$(b) \quad t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.95 \times 10^{-5} \text{ s}^{-1}} = 2.35 \times 10^4 \text{ s}$$

$$\ln[0.80] = -k(7.56 \times 10^3 \text{ s}) - \ln(1.0 \text{ M})$$

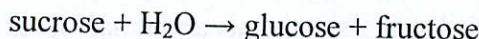
$$k = 2.95 \times 10^{-5} \text{ s}^{-1}$$

$$c \quad 24 \text{ hr} \times \frac{3600 \text{ s}}{1 \text{ hr}} = 8.64 \times 10^4 \text{ s}$$

$$\ln[A] = -(2.95 \times 10^{-5} \text{ s}^{-1})(8.64 \times 10^4 \text{ s}) + \ln(0.222 \text{ M})$$

$$[A] = 1.72 \times 10^{-2} \text{ M}$$

8. Hydrolysis of sucrose yields the simple sugars glucose and fructose:



The rate follows the rate equation: $\text{Rate} = k[\text{sucrose}]$ and has a half-life of $3.3 \times 10^5 \text{ s}$. If the initial concentration of sucrose is 0.10 M, what will be the concentration of sucrose after 24 hours?

$$\ln[A] = -kt + \ln[A]_0$$

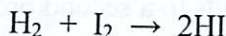
$$t = 24 \text{ hrs} \times \frac{3600 \text{ s}}{1 \text{ hr}} = 8.64 \times 10^4 \text{ s}$$

$$\ln[A] = -(2.1 \times 10^{-6} \text{ s}^{-1})(8.64 \times 10^4 \text{ s}) + \ln(0.1 \text{ M})$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{3.3 \times 10^5 \text{ s}} = 2.1 \times 10^{-6} \text{ s}^{-1}$$

$$[A] = 8.34 \times 10^{-2} \text{ M}$$

9. Consider the reaction of hydrogen with iodine:



This reaction has rate constants of $1.41 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ at 393°C and $1.40 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ at 443°C . What is the activation energy for this reaction?

$$T_1 = 393^\circ\text{C} = 666 \text{ K}$$

$$T_2 = 443^\circ\text{C} = 716 \text{ K}$$

$$\ln \frac{k_2}{k_1} = \frac{-E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

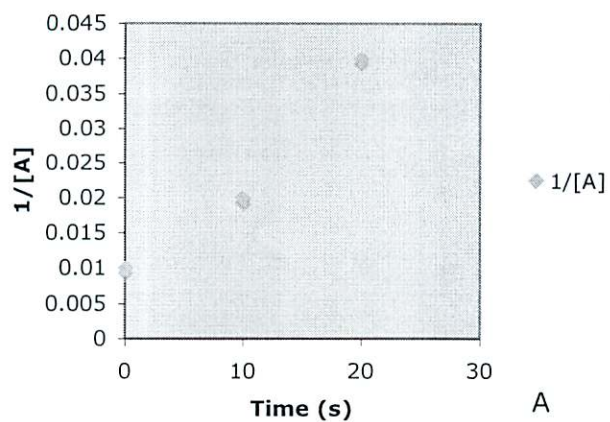
$$\ln \frac{1.40 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}}{1.41 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}} = \frac{-E_a}{8.315 \frac{\text{J}}{\text{mol K}}} \left(\frac{1}{666 \text{ K}} - \frac{1}{716 \text{ K}} \right)$$

$$E_a = 1.82 \times 10^5 \frac{\text{J}}{\text{mol}} = 182 \text{ kJ/mol}$$

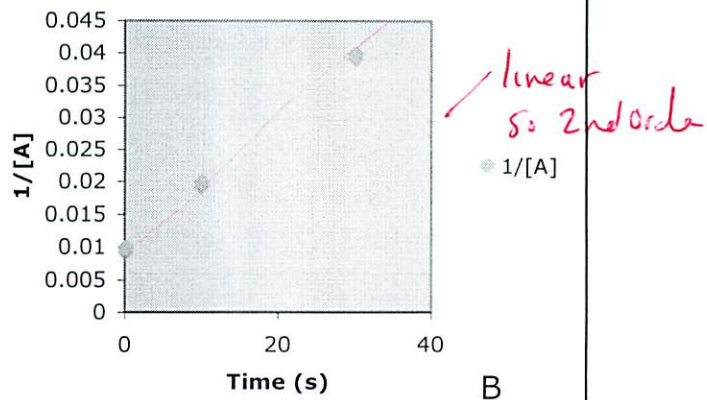
Problem 5

A			B			C		
[A](M)	t (s)	1/[A]	[A](M)	t (s)	1/[A]	[A](M)	t (s)	1/[A]
100	0	0.01	100	0	0.01	100	0	0.01
50	10	0.02	50	10	0.02	50	10	0.02
25	20	0.04	25	30	0.04	25	15	0.04

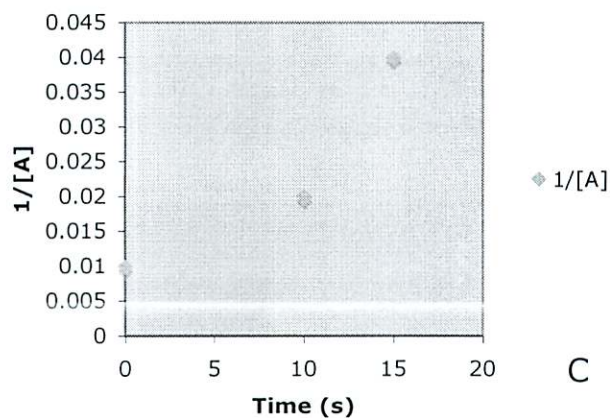
1/[A] vs. Time



1/[A] vs. Time



1/[A] vs. Time

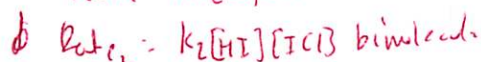
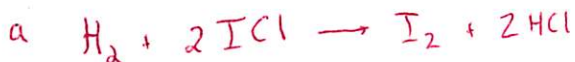


Reaction Mechanism Worksheets

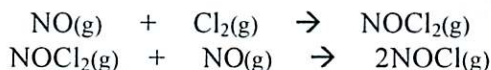
1. The following mechanism has been proposed for the gas-phase reaction of H_2 with ICl :



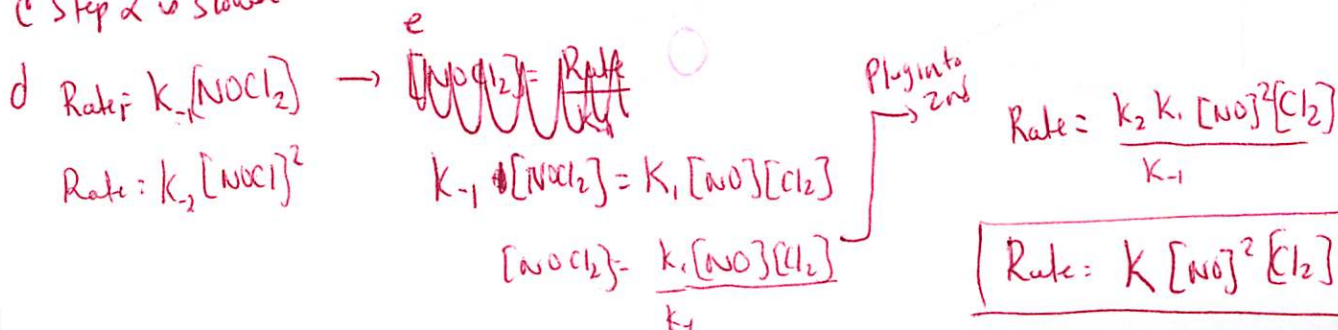
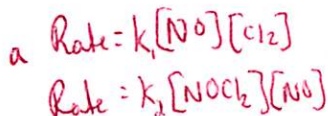
- Write the balanced equation for the reaction.
- Identify any intermediates in the mechanism.
- Write the rate laws for each elementary reaction as well as their molecularity for each step in the mechanism.
- If the first step is slow and the second one is fast, what rate law do you expect to be observed for the overall reaction?
- Sketch an energy diagram outlining each step in the reaction.



2. The reaction $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$ obeys the rate law, $Rate = k[NO]^2[Cl_2]$. The following mechanism has been proposed for this reaction:



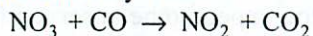
- Write the rate law for each elementary step.
- What would be the rate law be if the first step were rate determining? Does this match the rate law?
- What can you conclude about the relative rates of the two steps?
- Write the rate laws for the reverse reactions of each elementary step.
- Using these reactions derive the rate law for the overall reaction.



3. The overall reactions and rate laws for several reactions are given below. Of these, only _____ could represent an elementary step.

- A) $2A \rightarrow P$ rate = $k[A]$
☒ B) $A + B \rightarrow P$ rate = $k[A][B]$
 C) $A + 2B \rightarrow P$ rate = $k[A]^2$
 D) $A + B + C \rightarrow P$ rate = $k[A][C]$
 E) $A + 2B \rightarrow P$ rate = $k[A][B]$

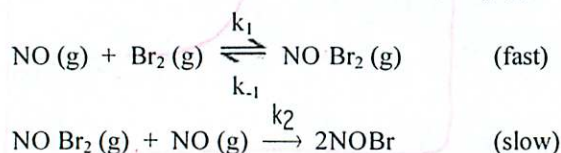
4. For the elementary reaction



the molecularity of the reaction is _____, and the rate law is rate = _____.

- ☒ A) 2, $k[\text{NO}_3][\text{CO}]$
 B) 4, $k[\text{NO}_3][\text{CO}][\text{NO}_2][\text{CO}_2]$
 C) 2, $k[\text{NO}_2][\text{CO}_2]$
 D) 2, $k[\text{NO}_3][\text{CO}]/[\text{NO}_2][\text{CO}_2]$
 E) 4, $k[\text{NO}_2][\text{CO}_2]/[\text{NO}_3][\text{CO}]$

5. A possible mechanism for the overall reaction, $\text{Br}_2(\text{g}) + 2\text{NO}(\text{g}) \rightarrow 2\text{NOBr}(\text{g})$ is



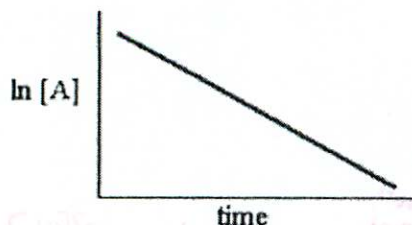
The rate law for formation of NOBr based on this mechanism is rate = _____.

- A) $k_1[\text{NO}]^{1/2}$
 B) $k_1[\text{Br}_2]^{1/2}$
☒ C) $(k_2k_1/k_{-1})[\text{NO}]^2[\text{Br}_2]$
 D) $(k_1/k_{-1})[\text{NO}]^2$
 E) $(k_2k_1/k_{-1})[\text{NO}]^2[\text{Br}_2]$

6. The rate law of the overall reaction $A + B \rightarrow C$ is rate = $k[A]^2$. Which of the following will not increase the rate of the reaction?

- A) increasing the concentration of reactant A
☒ B) increasing the concentration of reactant B
 C) increasing the temperature of the reaction
 D) adding a catalyst for the reaction
 E) All of these will increase the rate.

7. The graph shown below depicts the relationship between concentration and time for the following chemical reaction.



The slope of this line is equal to _____.

- A) k
 B) $-1/k$
 C) $\ln[A]_0$
☒ D) $-k$
 E) $1/k$